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σ/π versus π/π Conjugation: DFT Studies on Oligocyclopropenones and Related Systems

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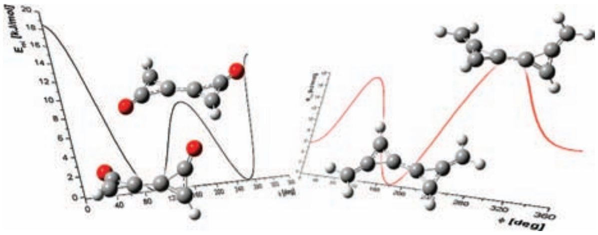
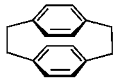
ABSTRACT



DFT studies on oligocyclopropenones and related systems 5(*n*)−9(*n*) are reported. A strong σ/π interaction between the π system and the σ framework of the three-membered rings is observed in almost all cases, leading to a perpendicular arrangement of the π systems in the most favored conformation. Also the shape of cyclic congeners is strongly influenced by σ/π interactions.

A simple and very useful concept in organic chemistry is the separation between σ and π framework within a molecule.[1] The geometries and the reactivities of numerous molecular entities can be explained by this approach.[1,2] The most prominent examples are ethylene and benzene where the σ system lies in the plane of the molecule whereas the π system is located out of the plane. The connection of two ethylene units **1(*1*)** leads to butadiene **1(*2*)** whose most stable conformation shows C_{2h} symmetry with an *s-trans* arrangement of the two CC double bonds. This planar conformation is favored due to efficient overlap of the p orbitals or in other words to an efficient π/π^* interaction between the two double bonds. However, in more complex molecules such as in [2.2]paracyclophane (**2**)[3] or strained bi-, tri-, and oligocyclic systems (e.g., **3** and **4**),[4,5] a hypothetical separation between the σ and π system does not suffice to describe their molecular properties and reactivities.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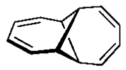
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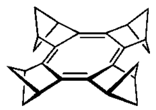
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In all of these cases we observe a strong interaction between the σ and the π system due to geometrical constraints.[3−5] In the case of **3** the two perpendicular π systems show a very large interaction via the σ system of its central four-membered ring.[4b,c] Cyclooctatetraene derivative **4** is planar due to an effective σ/π^* interaction between the bicyclic σ framework and the π system of the eight-membered ring.[5]

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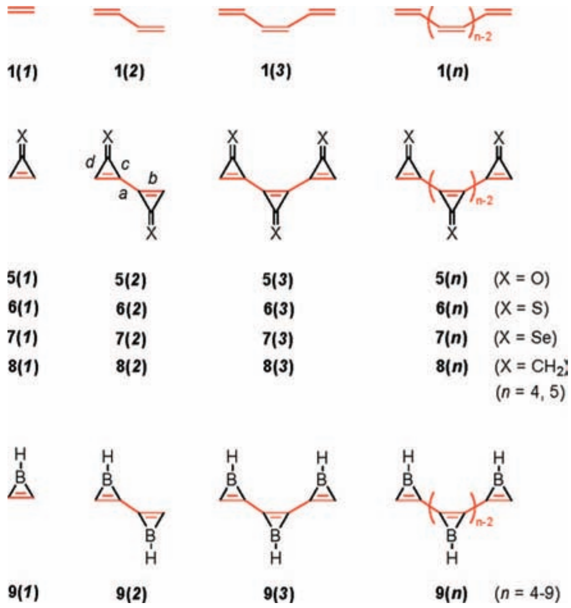
Commonly, the relative order of respective orbitals is the following: σ orbitals lie lower in energy than π orbitals, followed by π* and σ* orbitals. Thus, π orbitals overlap with π* orbitals most efficiently in a parallel fashion that we call conjugation, leading to an expanded *all-trans* arrangement of oligoenes **1(*n*)** in the most favored conformation.

Starting from this simple observation we raised the question whether potentially conjugated systems can be manipulated by electronic means in such a way that π/π conjugation is significantly reduced. We excluded steric constraints such as the use of bulky substituents to force the π systems in a perpendicular manner.[6,7] The idea was to use molecular units whose HOMO is of σ type (and in plane of the molecule) and whose LUMO is of π type (and out of plane of the molecule) or vice versa. The connection of two of these moieties shall lead to a most efficient interaction of σ- and π-type orbitals resulting in a perpendicular arrangement of the π systems of each unit.

It is well-known that the strained σ system of three-membered rings has two high-lying σ orbitals.[8] The relative energy of π* orbitals of olefins can be lowered by combining them with a π* orbital of a CO group (cf. 1,4-cyclohexadiene vs *p*-benzoquinone). Taking these considerations together leads to the assumption that cyclopropenone[9] moieties such as **5(*1*)** are potential candidates to construct such a molecular assembly. An evaluation of the frontier orbitals of cyclopropenone has shown that such a molecule fulfils these requirements (Figure 1). Substituted cyclopropenones[10−12] and also cyclopropenone derivatives[12d,13] were shown to be rather stable molecules; however, linked biscyclopropenones and derivatives thereof have not been elucidated by experimental or by theoretical means.

Figure 1. HOMO (left) and LUMO (right) of **5(*1*)** as calculated on the level of HF/6-311G(d) based on a B3LYP/6−311G(d) optimized structure.



Therefore, we investigated the geometrical properties of a series of linked cyclopropenones and congeners thereof by ab initio studies. All systems were optimized by DFT methods (B3LYP/6-311G(d)),[14,15] and the calculations were carried out with Gaussian 03.[16]

For all systems **5(*2*)−9(*2*)** we scanned the potential energy surface by varying the torsion angle φ (in steps of 10°,

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relaxed energy scan) between the planes of the three-membered rings. The results are shown in Figure 2. As anticipated by our previous assumptions, a stable conformation with an almost perpendicular arrangement of the two ring planes was found for **5(*2*)**, **6(*2*)**, **7(*2*)**, and **9(*2*)**. The corresponding rotational barriers leading to the C_{2h} and C_{2v} symmetric structures with conjugated π systems range from 1.2 for the selenium congener **7(*2*)** to 30.9 kJ/mol for **9(*2*)**. Only for **8(*2*)**, the congener with *exo*-substituted CC bonds, a linear arrangement (C_{2h} symmetry) as in the case of butadiene **1(*2*)** is more favorable (Table 1).

Table 1. Most Important Parameters of **5**(*2*)−**9**(*2*) for Minima and Maxima of the Potential Energy Surface (Calculated at the B3LYP/6-311G(d) Level of Theory)

		φ [deg]^a	a [Å]	b [Å]	c [Å]	d [Å]	ΔE_{rot} [kJ/mol]^b
5(*2*)	C_2	95.1	1.400	1.352	1.497	1.400	0.0
	C_{2h}	180.0	1.434	1.349	1.447	1.434	11.6
6(*2*)	C_2	107.6	1.399	1.341	1.460	1.401	0.0
	C_{2h}	180.0	1.418	1.340	1.437	1.420	4.0
7(*2*)	C_2	132.1	1.402	1.341	1.449	1.404	0.0
	C_{2h}	180.0	1.413	1.341	1.437	1.414	1.3
8(*2*)	C_2	96.9	1.417	1.323	1.462	1.430	14.8
	C_{2h}	180.0	1.409	1.330	1.455	1.431	0.0
9(*2*)	C_2	96.5	1.404	1.364	1.491	1.450	0.0
	C_{2h}	180.0	1.449	1.354	1.477	1.477	30.9

[a] φ describes the torsional angle between the two planes of the three-membered rings. [b] A value of 0.0 defines the global minimum.

A comparison of the distance a (for definition, see molecule **5(*2*)**) reveals short distances for $\varphi \approx 90°$ and longer distances for $\varphi = 180°$. These observations suggest that the σ/π^* interaction is much more efficient than the π/π^* interaction. Only in the CH_2 substituted system **8(*2*)**, π/π^* interaction seems to be more favorable, leading to an increase of bond length a for $\varphi \rightarrow 90°$ (Figure 3). In line with these observations the bond length c decreases when the planar C_{2h} symmetric structure is reached. A survey of all relevant bond lengths and the torsional angles φ for minima and rotational transition states of **5(*2*)**−**9(*2*)** is also given in Table 1.

NBO analyses[17] have shown that the Wiberg bond indices (WBI)[18] of the formal single bond between the three-membered rings of **5(*2*)**−**7(*2*)** and **9(*2*)** are much larger if the π systems are not conjugated. For **5(*2*)** a WBI of 1.14 is observed for bond a in the most stable conformer, whereas in the planar C_{2h} symmetric structure with conjugated π systems only a WBI of 1.03 is observed. This behavior is exceptional and stands in strong contrast to systems such as common linked π systems (e.g., **1(*n*)**, but also **8(*n*)**).

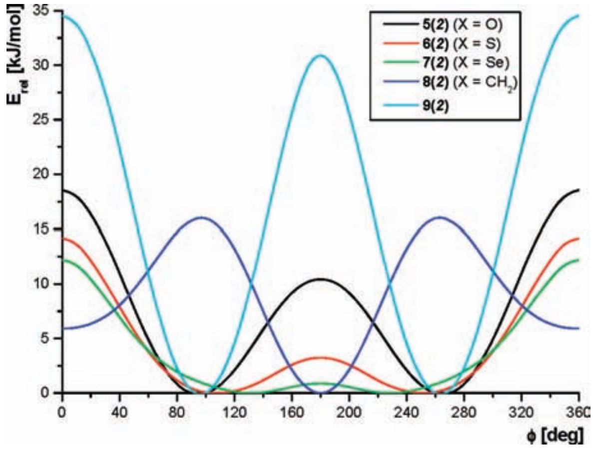

Figure 2. Scans of the rotational energies of **5(*2*)**−**9(*2*)** depending on the torsional angle φ as derived from B3LYP/6-311G(d) calculations.

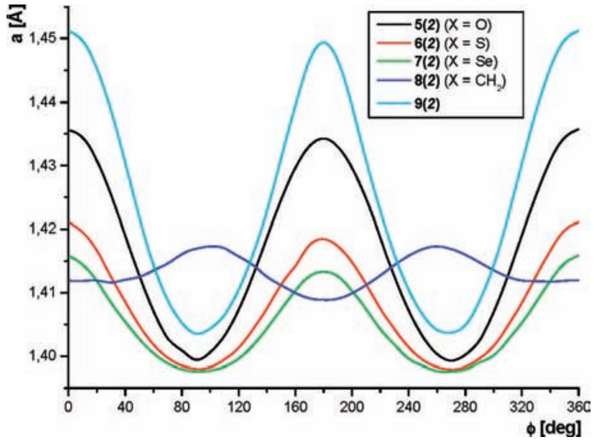

Figure 3. Variation of distance a in **5(*2*)**−**9(*2*)** depending on the torsional angle φ as derived from B3LYP/6-311G(d) calculations.

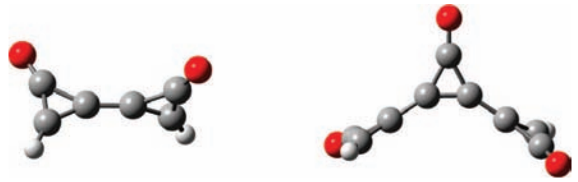

Figure 4. Most stable conformers of **5(*2*)** (left) and **5(*3*)** (right).

To unravel the various contributions leading to these unusual conformations, we used NBO analysis.[17] Such an analysis reveals that the magnitude of the rotational barriers results essentially as a compromise of two effects: the energetic difference between high-lying σ orbitals with the low-lying π^* orbital and the energetic difference between the π orbital of one unit and the π^* orbital of the other. A preference of the latter interaction forces the system into a planar arrangement as it is observed in the case of **8(*2*)**. For all other systems **5(*2*)**−**7(*2*)** and **9(*2*)** the principal interactions are $\sigma \rightarrow \pi^*$ interactions of the bent σ orbitals (bond c and

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to minor extent also bond *b*) with the unoccupied π^* orbital of the three-membered ring. Keeping these interactions in mind it is easy to understand the energetic order of the rotational barriers and the variation of the distance *a*. The more electron-withdrawing the CX (X = O, S, Se) or BH group is, the lower in energy is the π^* orbital. The bent σ orbitals are not that much affected by CX group, except in the case of **9(*n*)**. The electropositive nature of boron leads to a bent σ orbital even higher in energy than for **5(*n*)**−**7(*n*)**. Thus, **9(*2*)** shows the most pronounced effect of the series (Figures 2 and 3).

Besides the dimers we optimized also oligomers **5(*n*)**−**8(*n*)** ($n = 3-5$) (see Supporting Information). The most stable conformation of **5(*3*)** also resulting in a perpendicular arrangment of the π systems is shown in Figure 4. For the congener with the most distinct effect, **9(*n*)**, we elucidated the most favored conformations up to a 9-mer. As in Figure 5 depicted, one observes a helical structure consisting of three-membered rings, the result of the perpendicular arrangement of the π systems. Molecular orbital calculations have shown that the HOMOs and the LUMOs of these molecular entities are fully delocalized attributable to efficient σ/π interaction.

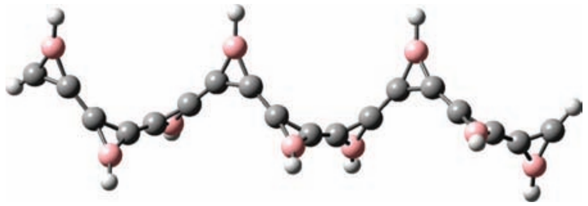
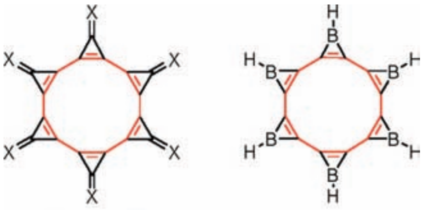


Figure 5. Optimized structure of **9(*9*)** showing a helical arrangement of the three-membered rings.

Finally, we analyzed the geometrical properties of cylopropenone hexamers and derivatives thereof arranged in a ring-like fashion, such as **10(*6*)**−**14(*6*)**. As anticipated from our previous results no planar structures were observed (with the exception of hydrocarbon **13(*6*)**). The binary carbon-chalcogen compounds **10(*6*)**−**12(*6*)** adopt a C_2 symmetric structure as depicted in Figure 6 for **10(*6*)**. In contrast, the BH containing counterpart **14(*6*)** shows an almost C_{2v} symmetric molecular structure. All of these calculations were performed without any symmetry restrictions. As anticipated from our previous investigations the hydrocarbon analog **13(*6*)** prefers planarity as a result of the more efficient π/π^* interaction.

In conclusion, our investigations demonstrate that oligocyclopropenones and corresponding derivatives are minima



10(*6*) (X = O)
11(*6*) (X = S)
12(*6*) (X = Se)
13(*6*) (X = CH_2)

14(*6*)

on the potential energy surface as shown by vibrational analysis. Most of their structures are determined by highly efficient σ/π interactions leading to C_2 symmetric conformations of the dimers with an almost perpendicular arrangement of the three-membered rings in the most favored conformation. This behavior is rationalized by high-lying σ orbitals being in the plane of the three-membered ring and low-lying π^* orbitals being out of plane. The double bond character between the π systems is larger for a perpendicular arrangement than for planarity. Synthetic efforts seem worthwhile to investigate these fascinating molecules and their remarkable conformations.

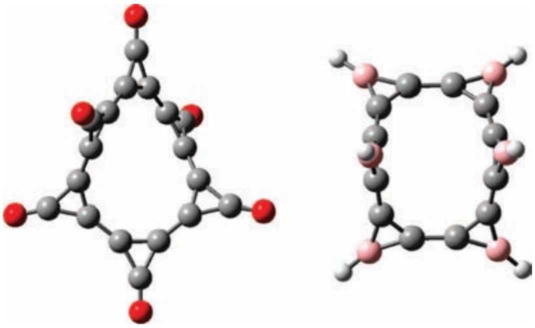


Figure 6. Optimized structures of **10(*6*)** (left) and **14(*6*)** (right).

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Supporting Information Available: Gaussian archive entries and optimized structures for all calculated species; overview of Wiberg bond indices. This material is available free of charge via the Internet at http://pubs.acs.org.

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